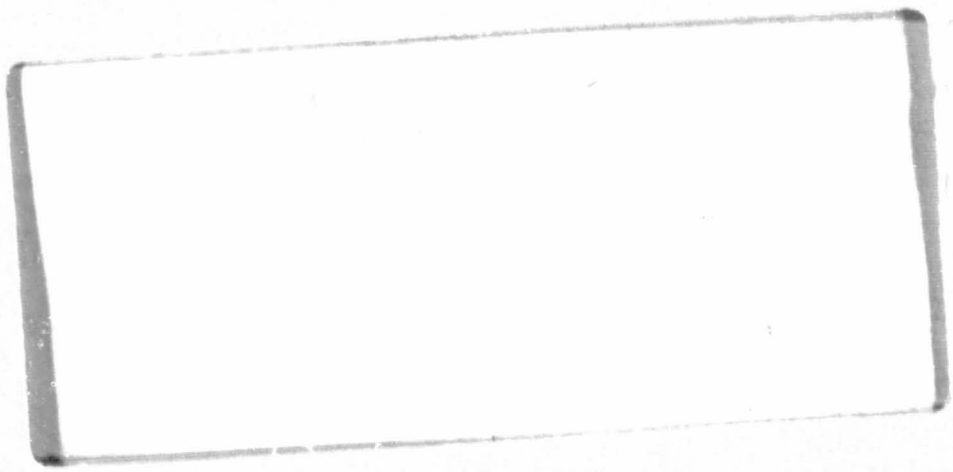

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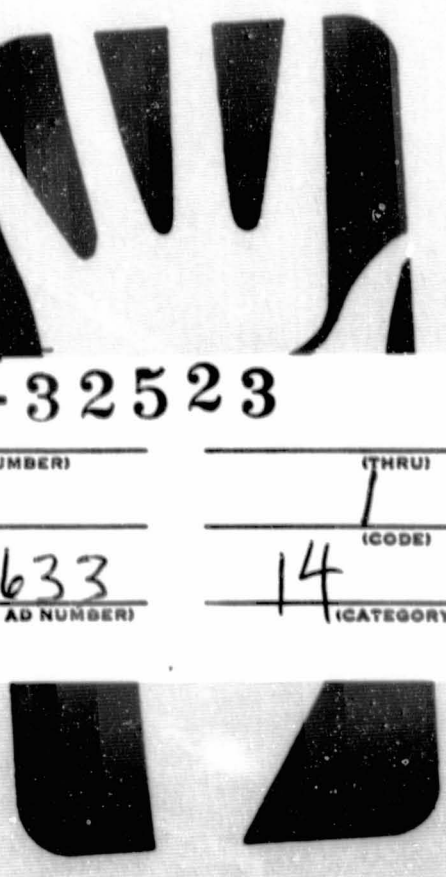

A Study on the Optimization of a Pyrolysis/Hydrogen Flame Detector System

FINAL REPORT

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ABSTRACT

Pyrolyzers, hydrogen flame detectors and supporting gas systems were investigated as part of a continuing program to develop a spaceworthy Pyrolysis/Hydrogen Flame Ionization Detector (FID) for use in an organic carbon detection system. Various configurations and arrangements for each subsystem of the FID were investigated at the outset. As anticipated, evidence gathered early in the program fully supported the belief that the operation of a sensitive FID unit on the Martian surface would require fundamental design changes in detector elements currently in use. The program accordingly evolved primarily into a study of the basic operational and performance characteristics of hydrogen flame ionization detectors. Theoretical studies and analyses were correlated with laboratory experiments in order to design and breadboard a pre-prototype detector. Results of the study were twofold. First, it achieved the unification of hydrogen flame ionization detector technology. Second, it produced an improved detector which ignites and sustains a flame at low pressures and is generally superior to the best commercial detectors available. Extension of this work should lead to a prototype flight detector suitable for various space missions.

I. INTRODUCTION

This document contains the findings and conclusions resulting from a research program conducted for the National Aeronautics and Space Administration by Analog Technology Corporation under NASA Contract NASW-1805, dated 17 September 1968. The program was directed toward the development of a Pyrolysis/Hydrogen Flame Ionization Detector for use in an organic carbon detection system on a MARS lander mission.

The purpose of preliminary life detection experiments on the initial MARS lander will be to detect and analyze life-derived organic matter in the soil. One of the most compatible experiments for this purpose is one utilizing a pyrolyzer/hydrogen flame ionization detector system. With this system, a mechanically-processed soil sample is injected into the pyrolyzer where it is heated in a closed atmosphere to a specific temperature. Organic matter in the soil sample is transformed to hydrocarbon vapor in an amount proportional to its concentration in the sample. The hydrocarbon vapor is transported to the hydrogen flame ionization detector (FID) which yields a signal proportional to the total number of hydrogen-carbon (C-H) bonds contained in the vapor sample.

The pyrolyzer/hydrogen flame ionization detector organic analyzer system is comprised of four functional subsystems: the sample injection system; the gas-handling and pneumatic system; the pyrolyzer; and the flame ionization detector. Each subsystem was investigated, and various configurations and arrangements were studied. However, the FID itself determines most of the design constraints of this

and the other subsystems and, to a large extent, establishes the overall performance characteristics of the analysis system.

Although preliminary studies were performed on the various subsystems, it was determined early in the program that operation of the FID in essentially a vacuum environment would require fundamental changes in existing detector designs. Thus, the program evolved primarily into a study of the operational and performance characteristics of hydrogen flame ionization detectors.

Basically, the FID portion of the study consisted of the following:

1. Literature survey and discussions with manufacturers of commercial FID's.

2. Detailed theoretical analysis of FID operating characteristics and mechanisms.

3. Correlation of the theoretical analysis with experimental results obtained from laboratory tests performed on several commercial detectors.

4. Extension of the theoretical analysis to the design of spaceworthy prototype detector.

5. Tests of the prototype detector.

6. Recommendations for further areas of investigation related to refinement of the detector into a completely spaceworthy FID.

The experimental study was conducted under two environments: standard conditions of temperature and pressure; and vacuum. Four commercial detectors were studied: Mino-Tek standard thermionic detector; Beckman GC-4; Perkin-Elmer 900; and Perkin-Elmer 226. Each of these detectors was characterized according to its respective current-voltage curves under the following parametric variations:

a) Voltage: 0-500 V

b) Hydrogen flow rate: 0-100 cc/min

c) Oxygen flow rate: 30-150 cc/min

d) Helium flow rate: 0-150 cc/min

e) Organic sample: methane in hydrogen at 0.2 and 5.0 mole percent.

f) Environmental pressure: 0-760 mm Hg

The pressure-ignition characteristics of the two Perkin-Elmer detectors, which provided the best basis for the evaluation of existing detectors, were as follows:

Perkin-Elmer 900

The ignition pressure limit was 250-300 torr with a 3-to-1 flow ratio of oxygen and hydrogen. Gas flow was reduced by a factor of 4 to achieve limit. Minimum hydrogen flow was 15 cc/min.

Ambient reduced pressure limit to sustain flame was 100 torr at a hydrogen flow rate of 15 cc/min. The flame was ignited at 760 torr and ambient pressure was gradually reduced. At 100 torr, the flame appeared diffused.

Perkin-Elmer 226

Ignition and flame reduced pressure limits were approximately 100 and 50 torr less than for the Perkin-Elmer 900, respectively. The flame detached at approximately 100 torr and was less severe with pure hydrogen. Detachment distance appeared to be a function of jet-tip temperature. At 45 torr, the flame was a blue haze surrounding the cathode. The hydrogen flow rate at 25 torr was approximately 30 cc/min. Larger flow rates undoubtedly due to the action of the detector chamber flow restriction. At 2 torr, the electrode was relatively hot due to catalytic combustion at the platinum surface. Increases in pressure to approximately 75 torr reignited the flame. With further increases, the flame reattached itself to the jet tip.

The analytical and experimental results demonstrated the magnitude of the problems at reduced pressure. Ignition and flame combustion in vacuum are possible only in a pressurized FID unit combustion chamber. A special pre-prototype detector for operation in a vacuum was therefore built to demonstrate the feasibility of operation. The sensitivity response of this detector at an environmental pressure of 1 atmosphere was 0.17 coulomb/g-atm C, which is superior to that of most commercial detectors.

The tests results at reduced pressures for the newly designed detector were:

(1) The detector sustained flames to environmental pressures of 3 torr.

(2) The detector ignited at all pressures and would sustain a flame below 200 torr with a cold detector.

(3) At detector temperatures higher than 170° C, reliable ignition was achieved and a flame was sustained at pressures to 3 torr.

II. THE HYDROGEN FLAME IONIZATION DETECTOR

A hydrogen FID is comprised of five functional elements: the flame; the ignitor; the collecting electrodes; the detector chamber; and the fuel and oxidant gases. The functional interdependence of these elements dictates the operational and performance characteristics of an FID unit. Thus, it became essential during the study to develop a basic understanding of the flame characteristics and their interaction with the remaining FID elements. This task became more difficult as the study progressed due to the absence of any unified treatment and/or thinking on the subject in the scientific community.

FLAME

There are essentially two types of flames which can be employed in this application, namely, premixed and diffusion flames. In a premixed flame, the hydrogen and oxygen gases are mixed in combustible proportions prior to burning at the jet tip exit. The mixing process in a diffusion flame is accomplished by a counter-diffusion mechanism of the combustion reactants and products at a region in the flame referred to as the reaction zone. Although each type of flame has distinguishing characteristics, the study showed that some characteristics are common to both flames. The diffusion region of premixed flames is located in the region surrounding the inner cone. The premixed region of diffusion flames is located on the outer surface at the base of the flame. Analytical and experimental investigations show that these dual properties are very important to the stability and combustion efficiency of the flames under reduced pressures.

Premixed flames are primarily characterized by the propagation velocity of the flame-front. The flame-front propagation velocity of a hydrogen-oxygen flame is approximately 20 cm/s. A stationary flame at the jet tip is, therefore, maintained by matching the gas velocity to the flame-front propagation velocity. A negative or positive velocity imbalance will result in the flame striking down the jet tip or flame detachment, respectively. The flame-front propagation velocity is also important in establishing the location of the detector ignitor, which will be discussed later.

Premixed flames are decidedly more turbulent and the flame noise is correspondingly greater, i.e., there is a significant variation in the ion production rate with time. This behavior reduces the signal-to-noise ratio of the detector. The largest part of the noise arises in the inner cone of the flame, while that of the diffusion region is relatively small. It is essential that premixed flames be provided with an atmosphere that can support the diffusion flame combustion. Otherwise, premixed flames exhibit poor combustion efficiency which, in a pressurized chamber, will result in periodic explosions similar to those experienced with internal combustion engines.

Thus, the single advantage of a premixed flame cannot be exploited in this application because, at a minimum, two separate gas supplies and streams must be provided to furnish the detector with a useable flame. The pneumatic subsystem cannot be simplified over that of a detector utilizing a diffusion flame.

Diffusion flames are more difficult to characterize, because no single set of parameters peculiar to this type exists. However, diffusion flame combustion may be adequately described by considering the mass and energy transport processes supporting the reaction. Diffusion flames are stationary in the sense that there is nothing about them that is remotely analogous to a flame-front propagation velocity. The combustion reaction occurs on a closed surface near the surface of the flame. Since the concentrations of hydrogen and oxygen molecules at the reaction zone are zero, a hydrogen and oxygen diffusion potential is established. The radial distance of the reaction zone from the axis of the flame is determined by the difference in the diffusion coefficients and, to a lesser degree, by the thermal effects introduced by the heat capacity and thermal conductivity of hydrogen, water, oxygen, and diluent molecules. At the reaction zone, water vapor is also diffusing outward. It should be noted that the diffusion process described above results more from eddy diffusion than from a molecular diffusion process. The height of a diffusion flame is related to other parameters by the expression

$$h \approx \left[\frac{q\, X_{H2}}{2\pi K X_{sH2}}\right]^{1/2} \qquad (1)$$

where h = flame height

q = hydrogen volume flow rate

K = thermal diffusivity

X_{sH2} = mole fractions of hydrogen in a stoichiometric mixture

X_{H2} = original mole fraction of hydrogen

The above equation is a simplification of the mass transport processes. However, the equation gives an indication of the effects of jet tip diameter and, to some extent, the introduction of helium as a fuel diluent. The mass and energy exchange at the reaction zone will be discussed in more detail in a later section.

Another important aspect of the diffusion flame is the premixed region at the base and its effects. The hydrogen-oxygen mixing is promoted by the negative pressure coefficient which is induced into the expanding hydrogen. Undoubtedly, there is local radial flow of oxygen at a rate exceeding the local rate of combustion. The properties of the flame at its base, therefore, are those of a premixed flame.

IGNITOR

The ignition of the FID flame is accomplished by adding energy to the combustible mixture at a sufficient rate to raise the temperature of the mixture to its kindling point (this ignition is accomplished only with a premixed flame). There are two fundamental types of flame ignitors which may be employed: a hot wire, and a spark ignitor. The two types differ only in the manner in which energy is introduced. Upon ignition of the

combustible mixture, a flame-front with a propagation velocity of approximately 20 cm/s radiates in all directions. This flame-front is extinguished only when it reaches a region where its composition is outside its flammability limits. The flame can also be extinguished if it traverses a region where energy is exchanged at a sufficiently high rate from the flame-front to the surroundings so that a drop in temperature below its burning temperature occurs. (Examples of this phenomenon are the operation of flame arrestors and safety lamps of the type used by miners.) The relationship between the flame-front energy transfer rate and extinction of the flame is characterized by a parameter called the gas-quenching volume or diameter. Several experimental arrangements can be employed to measure the gas-quenching volume. The one most commonly utilized is the flat-plate propagation volume where a flame-front propagates through the cavity. The plates are moved closer and closer together until it is impossible to transport the flame through the cavity. The perpendicular distance separating the two plates is the quenching diameter of the flame. This means that the electrode system surrounding or adjacent to the flame must be designed to prevent quenching of the ignition flame. Further study showed that a reliably-igniting detector will operate at cross-purposes to an efficient ion collection system. Thus, a flame completely enclosed by an ion collecting surface will quench the ignition flame-front when its effective separation is less than the quenching diameter of the gas mixture.

The quenching diameter is the function of gas total pressure which was found to be inversely proportional to

the cube of absolute pressure. A detector operating at a total pressure of 1/2 atmosphere will require a minimum electrode spacing eight times larger than that of a detector operating at 1 atmosphere. It is obvious that there will be separation limits placed on the electrode system other than those imposed by thermionic emission. It is possible that only a minor reduction in flame noise can be accomplished by shrouding the flame because of the ignition reliability problems. Some of these problems may be alleviated by operating at a higher pressure which will induce larger and more severe free-convection currents as will be discussed later.

The most reliable ignition element which may be employed in this application is a hot wire surface. It is superior to a spark ignition system, because the associated equipment and elements required to produce the high temperature surface are simpler than those of a sparking system. Also, recharging and discharging of condensers will not be required. An added reliability factor can be included with a hot wire ignitor by fabricating the hot wire of a material which will promote catalytic combustion. The most likely catalytic materials are platinum and palladium. In the event that the ignitor heating system fails, the heat of reaction produced by the catalytic combustion of hydrogen and oxygen on the catalytic surface is sufficient to raise its temperature to that required to ignite the gas mixture.

Aside from the quenching problem, it was experimentally demonstrated that the location of the ignitor surface may be important in the design when not maintained within given limits.

The velocity of the combustible gas mixture at any point between the ignitor surface and the detector jet tip must never exceed the propagation velocity of the flame-front. In fact, the velocity should be much less in order to assure reliable ignition. The flame-front velocity is approximately equal to the velocity of the gas at the jet tip. Deviations from this equilibrium condition will allow the flame to strike back down the detector jet tip or the flame will detach itself and stabilize at some position above the jet. The equilibrium position is determined by the exchange of the gas from the jet tip. As the gas expands, the velocity is reduced to the point where it is equal to the flame-front propagation velocity. This discussion applies only to diffusion flames because of the premixed nature of a diffusion flame.

The location of the ignitor surface is also important from the standpoint of ignition explosion. It can be seen that, as the ignitor surface is moved away from the main gas stream, a more or less homogeneous mixing of hydrogen and oxygen will occur throughout the volume of the chamber. Thus, a large pressurized chamber with the ignitor at a relatively large radial distance from the jet tip could easily ignite with a violent explosion. It is not desirable to permit ignition in this fashion, unless the chamber length-to-diameter ratio is within specific limits.

The temperature of the ignitor wire is ordinarily maintained at several hundred degrees above the ignition temperature of the gas. The wire temperature is established by the heat transport properties of the gas mixture, the surface area of the wire, and the velocity of the gas. More accurately, the temperature of the ignitor is related to Nusselt, Prandtl,

and Reynolds numbers. The gas velocity, density, and other properties can be related to the geometry of the ignitor and the final burning temperature as

$$T_b = \frac{\frac{E}{2R}}{\ln\left[(B/A)^2 \frac{D}{W} \gamma\right]} \qquad (2)$$

where T_b = final burning temperature

E = activation energy of the chemical reaction

R = gas constant

γ = kinematic viscosity

D = diameter of the wire

W = rate of reaction (burning)

B & A = constants related to the reaction order ($B=1/2$, $A=1$ for $H_2=1/2\ O_2=H_2O$

Equation (2) is utilized in the heat balance relationship at the ignitor surface relating the dimensionless moduli cited above.

$$q = \frac{A\mu}{D} (Pr)^u (Re)^m (T_i - T_k) \qquad (3)$$

where q = ignitor power

A = ignitor surface area

μ = gas mixture viscosity

T_i = ignitor surface temperature

T_k = burning temperaute

Pr = gas mixture Prandtl number

Re = gas mixture Reynolds number

u & m = constants depending upon temperature and Reynolds number range

Equation (3) is used to compute the ignitor power requirements. The local Reynolds number adjacent to the ignitor surface should be used in this noted equation.

COLLECTING ELECTRODES

The design of the collecting electrodes must incorporate features which provide maximum sensitivity and, at the same time, promote aerodynamic conditions to prevent the internal circulation currents in a pressurized combustion chamber from disturbing the flame. Also, the electrode spacing or diameter in the core of a cylindical electrode must be greater than the quenching diameter of the gas mixture ($\simeq$ 0.1 @ 1 atm).

The electrode efficiency and collecting characteristics can be assessed by utilizing the sensitivity parameters

and the I-V properties. The sensitivity is the measure of the total number of coulombs collected by the electrode for every g-atm of carbon through the flame, i.e., coulombs/g-atm. At atmospheric pressure, utilizing optimum flow rates of hydrogen, helium and oxygen, the sensitivity parameter is near 0.2 - 0.5. The shape of the detector current-voltage curves in the plateau region and/or the voltage of the knee can also be employed to establish the degree of competitive collection, thermionic emission, ion blow-by and, in some cases, the detrimental influences of the space charge. An I-V curve with a positive linear slope in the plateau region is characteristic of thermionic emission. An I-V curve with a negative slope in the plateau region is characteristic of competitive collection. An I-V curve without a knee or plateau but with a positive low-level slope ordinarily indicates ion blow-by. All the detectors investigated were characterized in this manner.

In order to establish the electrode system's theoretical performance limits and the relative importance of its parameters, an investigation of the electrode process was conducted. The results of the study will be exceedingly valuable in the design of the electrode system for the flight prototype detector.

Ion blow-by and space charge effects may establish the electrode geometry and, perhaps the oxygen flow rates. It is anticipated that the ion collector may approximate a hollow, small-diameter (D = 0.1 cm) cylinder which completely surrounds the flame over its entire length. The jet tip could be the electron collector. The oxygen will flow through the cylinder and prevent or minimize the effects of circulation within the chamber. Care must be exercised to maintain a favorable oxygen flow condition (Re < 100).

It was analytically determined that the space-charge problem which can assert itself is chiefly concerned with the electrode geometry. Since the flame is a relatively good conductor, the electric field in it is zero and the small voltage drop is due only to ohmic drop. Therefore, the ion currents are diffusion-limited and can be expressed by:

$$I = SN_+ e\sqrt{\frac{KT_+}{2\pi M}} \qquad (4)$$

where

I = ion current

S = area of the electrode surface sheath established by the space charge

N_+ = average ion concentration in the flame

e = electronic charge

K = Boltzmans constant

T_+ = ion temperature as defined by Langmuir probe experiments

M = ion mass

In cases where the inside surface of small-diameter cylindrical electrodes are employed, it was observed that the diffusion-limited current as defined by equation (4) is a decreasing function of electrode voltage. This behavior is primarily due to the increase in the electrode

sheath thickness with voltage. Thus, when utilizing the inside surface of a cylinder, the diffusion area (S) is reduced by a corresponding amount.

THE DETECTOR CHAMBER

The primary design considerations of the detector chamber were those associated with its temperature, water condensation, and aerodynamic properties.

The chamber design incorporated features which provided a minimum disturbance to the flame and permitted the detector chamber to reach temperatures near 110^{o} C as rapidly as possible in order to prevent water condensation in the pressurized unit. Specially-located dead-volume chambers and/or circulation baffling systems may also have to be provided to dampen the circulation currents.

III. DETECTOR SENSITIVITY AND FLAME NOISE

The detector sensitivity and flame noise are related to the ionization process in the flame. The detector sensitivity can certainly be increased by factors nearing 100 by altering the ionization kinetic parameters. The noise of flames burning in a pressurized chamber is of large amplitude and relatively low frequency (2 - 3 Hz). It is also believed that the flame noise can be attenuated to some degree by controlling the kinetic parameters of the flame.

IONIZATION MECHANISM

The process by which ions are formed in flames has been in dispute for several years. However, it has been quantitatively described as a chemi-ionization process. Several theories based on specialized energy exchange processes due to thermal energy transfer could not be used to prove that sufficient energy is available to produce the number of ions which had been measured in flames. Other theories related to impurities arising from carbon particles, sodium, potassium, and other elements have also met with failure in this respect, that is, the number of ions produced does not nearly match the concentration level measured by experiments.

The chemi-ionization process explains both the qualitative and quantitative aspects of the mechanism.

It is believed that sufficient energy is imparted to a given number of hydrocarbon molecules existing in the complex activated state to induce a transition to the ionized state of approximately 13.29 eV. The concentration level of hydrocarbon ions predicted by this method is approximately that found by experimental means, which is 1×10^{10} ions per cc. These considerations show that only a very small fraction of the total number of hydrocarbon molecules available is ionized. The mole fraction is approximately 10^{-6}. This discussion indicates that a hydrogen flame ionization detector can be made more sensitive to the detection of hydrocarbon molecules only by increasing the fraction of ionized hydrocarbon molecules. In many respects, some apparent sensitivity can be realized by increasing the fuel flow rate to the detector. This technique, however, is usually misleading for continuous measurements, primarily because the amount of sample increases with the hydrogen flow rate. In special applications where a pyrolyzed sample of hydrocarbon is injected into the hydrogen stream, the total number of coulombs produced is proportional to: the total number of hydrocarbon molecules ionized; the concentration of hydrocarbom molecules that have been pyrolyzed; and a combination of these two things. The total number of hydrocarbon molecules ionized from a given sample is proportional to the structure and temperature of the

flame. Since a diffusion flame is best suited for flame ionization detectors, the structure of the flame may be characterized by the total area of the flame reaction zone. Some errors are introduced in applying this rule because a vertical concentration gradient of ions which is a function of the flame height, exists in the reaction zone.

At a reduced pressure of about 0.5 atmosphere, the ion concentration for the steady-state condition may change by a factor of 3, with the greater concentration of ions existing near the jet tip. Several means by which the flame structure can be altered to produce a larger reaction zone surface area are available. The most common technique employed for commercial applications is the use of helium gas as a fuel diluent. Detector sensitivity has been increased by an order of magnitude by diluting the hydrogen with approximately one-third helium. The sensitivity of the detector was increased from 0.02 coulomb/g-atm C to 0.2 coulomb/g-atm C.

Again, this increase in sensitivity is accomplished by altering the structure of the flame reaction zone. Not only is the area of the reaction zone increased but there is sound evidence that the reaction zone becomes more diffuse or thicker with the amount of helium in the fuel. The sensitivity ordinarily increases with the

addition of the helium until a peak sensitivity is reached; beyond this, the further addition of helium causes a decrease in sensitivity. Sensitivity decreases are caused primarily by a reduction in temperature of the reaction zone due to its having a higher thermal conductivity than that of water vapor and oxygen.

The transport properties of hydrogen and helium are relatively similar when compared to oxygen, nitrogen, carbon dioxide and water vapor. Therefore, it is apparent that the primary changes introduced by helium are effective only in the product side of the reaction zone. Aside from the fact that an additional amount of inert mass must be heated to the reaction temperature by the heat of combustion, the thermal diffusivity and the diffusion coefficient on the product side are greatly altered. Hydrogen, helium and the ordinarily small amount of hydrocarbons and some impurities diffuse from the core of the flame into the reaction zone. On the product side, water vapor, CO_2, unburned hydrocarbons and intermediate products diffuse away from the reaction zone and the oxygen diffuses toward the reaction zone. Helium, when present in the hydrogen stream, also diffuses away from the reaction zone on the product side. The presence of helium very definitely alters the properties of the system on that side of the reaction zone. The thermal conductivity of helium is

approximately 10 times greater than that of the other gases present and its diffusion coefficient is approximately 5 times greater. Its heat capacity is also 5 times greater.

A quantitative description of the kinetic changes introduced by helium can be described by considering the mass and energy transport mechanisms in the system. Most of the changes occur on the product side of the reaction zone. However, the increase in the total surface area of the reaction zone is induced by the difference in the diffusion coefficient of helium and hydrogen in water vapor as opposed to the diffusion coefficient of water vapor in hydrogen. Also, it is apparent from dilution considerations alone that a larger area with a greater transport distance will be required to attain a stoichiometric mixture with hydrogen and oxygen. This transport distance is a logarithmic function of the flame reaction zone radius, the diffusion coefficient of helium in hydrogen, and temperature. The sensitivity is also increased by a factor proportional to the increase in the height of the flame. The increases in sensitivity due to the flame height are also reflected in the increases in reaction zone area and are approximately equal to the radial increases.

Further analytical investigation was conducted to establish the feasibility of increasing the detector sensitivity by increasing the flame reaction zone area, such as with a flat flame possessing a large aspect ratio. Calculations demonstrated this feasibility, as well as revealing the fact that this approach offers distinct advantages in the ion-collection efficiency of

the electrodes. However, for the relatively low-volume flow rates in an FID, there is no aerodynamic difference between conical and flat flames for aspect ratios of 20 and below. It was concluded that aspect ratios greater than 100 were required to fully exploit the advantages of a flat-flame. The approximate dimensions of a flame holder for this aspect ratio would be 0.635 cm by 0.0635 mm. A flat flame holder utilizing these dimensions was fabricated and tested. The volume flow rates and Reynolds number were equivalent to those of the jet tip in the GC-4 detector. It showed a sensitivity parameter of one-half that of the conical. However, it was later established that approximately 90% of the sample was lost through leaks. Attempts to seal the flat-flame holder failed. The test results, nevertheless, were very encouraging.

FLAME NOISE

There are ordinarily two mechanisms which contribute to the detector signal-to-noise ratio. Associated with the normal pyrolyzed sample is a blank noise reading which is as yet not satisfactorily explained. The signal current normally associated with the blank reading is approximately 10^{-12} A. This level varies considerably with the thermal history of the pyrolyzer-sample injector system, the cleaning procedures employed, and, in some instances, the particular geographic region of operation. The blank background current level must be quantitatively explained in order to promote more accurate sample determinations. Several theories attempting to explain the properties and sources of the blank have recently been proposed.

The theory gaining most popular favor is that associated with a contamination process which arises from adsorbed molecules on the surface of the kinetic elements of the system. Regardless of the source, the nature of the impurities remain unexplained. For example, hydrocarbon impurities would seriously limit the sensitivity of the detector, because procedures implemented to increase the current level will also increase the signal-to-noise ratio of the detector, that is, amplification of the current level would also promote amplification of the blank background level. A simple test can be devised to identify the hydrocarbon origins of the impurities. If, indeed, the impurities are hydrocarbons, then it is probable that only a small fraction of the total number are ionized in the flame. Thus, the addition of helium to the fuel hydrocarbon mixture would certainly ionize a greater fraction in the flame. To relate the background blank current level to the helium flow rate into the detector would be a simple matter.

Another proposal suggests that the blank current level may be due to potassium and sodium impurities. The fraction of potassium and sodium molecules ionized in the hydrogen flame is almost complete. Thus, additions of helium and any other means which may be employed to increase the flame reaction zone surface area would not produce an increase in the blank background current level.

Another anomalous characteristic of the blank reading is its lack of consistency. Contamination by hydrocarbons in the preceding samples would probably not produce these variations. The adsorbing and deadsorbing properties of

of the construction materials used in the pneumatic and sample-handling systems of the FID unit are primarily well established and their characteristics well-known.

A more serious source of flame noise arises from the aerodynamic disturbances in the FID chamber as mentioned earlier. A hydrogen flame is usually operated in the laminar flow region well below a Reynolds number of 2200. The commercial hydrogen flame detectors investigated in this study all operated below 320. Thus, flame noise due to disturbances between the flame and the supporting atmosphere is minimized. The aerodynamic noise is that induced by gas circulation currents in the detection chamber which become more severe as the pressurized chamber vent is reduced in size. For a pressurized detector such as that operating in a vacuum, the equilibrium vent diameter is approximately 0.010 inches, and erratic unpredictable aerodynamic disturbances ensue. The flame noise arises from the interaction of the flame with the recirculating gas. Changes in the flame reaction zone surface area are induced. Under ordinary near-steady-state conditions, a low-frequency, large-amplitude noise has been observed in the pressurized detector. It is important that the detector chamber include baffling surfaces and recirculation subchambers. This arrangement can plausibly be promoted by locating the flame in a relatively high velocity region of the oxygen. It will minimize the effect of the free-convection currents which constitute the driving mechanism of the circulation.

Determination of the flame noise level, after the aerodynamic disturbances have been minimized, will establish

the maximum signal-to-noise ratio of the detector. Obviously, if the signal-to-noise ratio of a detector, considering only the aerodynamic flame noises, is smaller than the signal-to-noise ratio of the detector established by the blank current level, a study of the characteristics of the blank noise would be superfluous. However, if the converse is true, we should then study the possibility of establishing the characteristics and sources of the blank in order to reduce it to a level comparable to the signal-to-noise ratio of aerodynamic flame noise.

IV. OPERATION AT REDUCED PRESSURES

The FID performance is established by the atmospheric pressure constraint. The functional dependence is fundamentally ascribed to pneumatic conditions defined by the hydrogen-helium, oxygen, and atmospheric pressures. Operation of an FID unit designed for relatively high atmospheric pressure specifications, e.g., 760 torr, is not possible below certain reduced pressures without major changes to the flame chamber and/or implementation of gas flow and pressure controls.

A typical situation arising with commercial FID units is that which develops as the atmospheric pressure is reduced. As the H_2-He to atmospheric pressure ratio exceeds the critical pressure ratio, the linear velocity of the gas at the jet exit is equal to the acoustic velocity. Gas flow conditions at Mach one evidently do not permit the operation of an FID unit. The gas velocity at the jet exit will be approximately 200,000 cm/s and the Reynolds number, 31,200. These are clearly turbulent flow conditions. The Reynolds number should be below 2,000 and is usually maintained below 100. Thus, the Reynolds number must be reduced by a minimum factor of 200. Assuming the flame can be ignited and that the gas at the jet exit is at 1,000^{o} C, the Reynolds number will be reduced by a factor of 2.5 to 12,500 by gas viscosity increases. The diameter of the jet exit may be reduced but only by also reducing the flame diameter. The most effective way to reduce the Reynolds number is apparently by reducing the gas flow rate and delivery pressure.

For operation at an atmospheric pressure of 5 millibars, the delivery pressure must not exceed 10 millibars to prevent

a choked condition at the jet exit and 6 millibars to produce favorable gas flow and pressure conditions. A relatively low gas flow rate will result. Thus, a small flame with a correspondingly small signal will be produced. A flat flame can be employed to advantage in this application to increase the signal and stabilize the flame. Other problems exist in igniting the FID. Aerodynamic, chemical, and heat-transfer effects affect the ignition characteristics at reduced pressure to compound the problem. As reported earlier, a combustible mixture or only a premixed flame can be ignited. Thus, the gas velocity at the ignitor surface or the region adjacent to the reaction zone of the diffusion flame must never exceed the flame-front propagation velocity of the premixed flame. The flame propagation velocity has been estimated never to exceed 20 cm/s. Therefore, the velocity profile of the expanding gas jet must be controlled to a degree where ignition of the diffusion flame can be achieved. Thus, the flame will detach itself from the jet tip due to excessive gas-jet velocity. Also, a relatively large degree of fuel and oxidant mixing will occur in the transition region where the gas velocity decreases. The ion concentration gradients normally experienced with diffusion flames will be distorted. The degree of flame detachment will prohibit using the jet tip as the positive electrode because of the relatively large distance the electrons will be required to traverse despite their large mobility. All these processes determine the critical location of the ignitor within the FID chamber.

The 5-millibar reduced pressure condition appears to have excluded the possibility of igniting the commercial detectors at our disposal. Calculations also indicated the FID would be outside the flammability limits for ignition.

The gas velocity appears to be greater than the flame-front propagation velocity in the region of the ignitors. The ignitors of the detector had to be altered to permit changes of their effective location. Higher ignitor surface temperatures were required to supply sufficient power for ignition. An increase in the ignitor surface area would have helped for identical reasons. It is also possible that the flame will extinguish itself if the direction of flame propagation is not correct. This condition arises when the relative position of the ignitor and reaction zone of the diffusion flame permits flame propagation in the direction of a lean combustible mixture only. This possibility is enormously increased with detached flames possessing relatively large premixed regions.

Some of the problems in reduced-pressure operation were alleviated by restricting the gas flow from the combustion chamber to the atmosphere. The FID would operate at higher gas pressures and gas flow rates. It was analytically determined that other problems, however, are introduced with this design. At 5-millibars pressure, the boiling point of water is 1^{o} C. Pressurization of the chamber increases the boiling point, e.g., at 50 millibars, the boiling point is 39^{o} C. The temperature of the chamber walls and all components must be maintained above the water boiling point to prevent condensation. These problems were experienced with one of the commercial detectors whose flow from the chamber is restricted to only a small degree. The amount of restriction required for this application will probably be much greater. It is likely that the chamber can be heated above the boiling point and maintained at a given temperature with only heat of combustion. Nevertheless, the commercial

detectors studied were equipped with heating elements and temperature indicators and controls for the warmup phase.

Another problem associated with flow restriction of the chamber is that of reaching chemical equilibrium of the combustion products in the chamber within a reasonable time. The partial pressure of water vapor will constantly change until equilibrium is attained. During this time, flame temperatures drop and the FID response changes continually. It is not certain to what extent this condition will affect the signal in time.

V. TEST RESULTS OF IGNITION AND COMBUSTION AT REDUCED PRESSURES

Experimental investigation of commercial FID operation at reduced pressures demonstrated that combustion, ignition, ion distribution, and structural characteristics of flames are considerably altered by operation at reduced pressures. Also, the pneumatic conditions arising at reduced pressures promoted turbulent noisy flames. At sufficiently reduced pressures, it is not possible to initiate flame ignition and sustain flame combustion. Analytical and experimental investigations show that approximate ignition and combustion-reduced pressure limits are 200 and 100 torr, respectively.

TEST APPARATUS

The test equipment and configuration required to obtain maximum information from test results is of great importance. Therefore, the equipment used to support this study is described according to the major classifications of test functions.

Gases

Matheson high-grade chromatography gases were utilized to insure accuracy. Ultra-pure oxygen, hydrogen and helium were used to perform precise blank current measurements. Hydrogen diluted with 5% or 2/10% methane was used to measure detector efficiencies with simulated steady-state samples.

Filters

Chemical Research Corporation Dririte-desiccant filters were placed in all gas lines to assure minimal

contamination due to handling. These filters were specifically designed to remove moisture and oil.

Valves

Matheson high-grade chromatography metering valves and Hoke chromatography toggle valves proved to be excellent for highly sensitive control of gas systems.

Regulators

Matheson high-grade chromatography regulators provided accurate control of delivery pressure for all gas lines.

Flow Meters

Matheson predictability flow meters were used in conjunction with adjustment curves compensating for the type of gas, temperature, and pressure.

Pressure Monitors

Two types of pressure detection systems were applied. A Cenco mercury manometer was used to monitor pressures with absolute values less than one atmosphere. Sensitive Consolidated Electro-Dynamics potentiometric pressure transducers were used to monitor pressures with absolute values from one to three atmospheres.

Vacuum System

The vacuum system consisted of a Cenco Hy-Vac mechanical and diffusion pump. Ajean Vac-Tronics feedthroughs and seals aided in obtaining a well-defined subatmospheric environment.

Plumbing

Swagelok, Tylok and Gyrolok gas fittings and tubing were used in all plumbing applications.

Electrometer

An ATC-designed and -tested electrometer monitored detector currents. This solid-state electrometer was chosen because of its high input impedance, low noise, fast response and mechanical range switching capabilities.

Thermocouple System

Ice-bath-referenced, iron-constantan thermocouples with a potentiometric readout were used for temperature monitoring.

Power Supplies

In general, it was possible to use standard laboratory supplies. Two special applications required a 6-V high-current supply and a Power Design 5005 precision millivolt source. The 6-V supply was used for the hot wire ignitor and consisted of a Variac and a 6-V filament transformer.

Detectors

Beckman GC-4, Perkin Elmer 900, Perkin Elmer 226, and Mino-Tek standard detectors were used.

IGNITION AT REDUCED PRESSURES

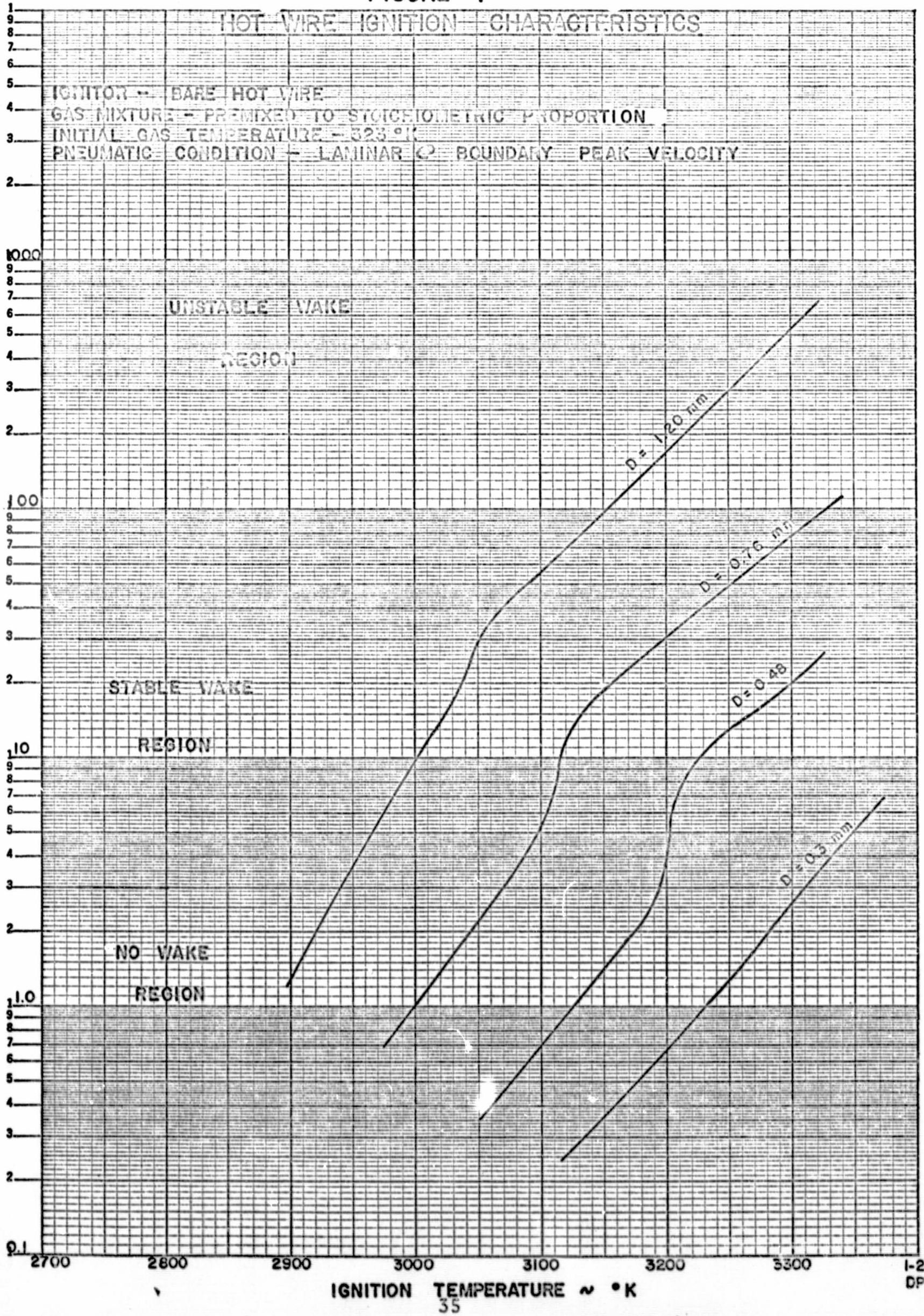
Ignition of a diffusion flame is accomplished by heating a given minimum volume of gas in one of its premixed

regions to its ignition temperature. The premixed regions include the area at the base of the flame near the rim of the jet tip or an area downstream where sufficient hydrogen and oxygen mixing has occurred by a diffusion process.

Ignition failure may result because the supply of ignition power to the premixed quenching volume is insufficient (the combustible mixture at the ignitor being outside the compositional flammability limits), and because the gas velocity exceeds the flame-front propagation velocity at any point between the ignitor surface and the reaction zone of the flame.

The minimum power requirements for ignition are related to the ignition surface temperature and its exposed surface area. Figure 1 illustrates the relationship of these parameters to the premixed gas Reynolds number at the ignitor. As Reynolds number is increased, the surface temperature of a hot wire ignitor must be correspondingly increased to provide sufficient ignition power to the quenching volume. Higher temperatures are required to transmit the power because the contact time of a gas particle with the hot surface is reduced as Reynolds number is increased. Figure 1 also illustrates the importance of the pneumatic conditions and position of the ignitor within the FID chamber. It must be located in a region where the Reynolds number of the combustible mixture never exceeds the limit defined by the wire diameter. Also, a combustible mixture must surround it and a combustible mixture path between the ignitor and the jet tip must exist. An important aspect, not directly shown in Figure 1, is that the gas velocity must never exceed the flame-front propagation velocity.

FIGURE 1


HOT WIRE IGNITION CHARACTERISTICS
IGNITOR -- BARE HOT WIRE
GAS MIXTURE - PREMIXED TO STOICHIOMETRIC PROPORTION
INITIAL GAS TEMPERATURE - 323 °K
PNEUMATIC CONDITION - LAMINAR @ BOUNDARY PEAK VELOCITY
UNSTABLE WAKE REGION
STABLE WAKE REGION
NO WAKE REGION
D = 1.20 mm
D = 0.76 mm
D = 0.48
D = 0.3 mm
REYNOLDS NUMBER
1000
100
10
1.0
0.1
2700
2800
2900
3000
3100
3200
3300
IGNITION TEMPERATURE ~ °K
5 CYCLES X 70 DIVISIONS
1-22-69
DPL/gs

At reduced pressures, the converse is quite likely true when the gas flow rates, hydrogen Reynolds number at the jet tip, and Mach number at the jet tip are not interrelated in a specified manner and maintained within prescribed limits. The conditions become unsatisfactory at the point where the chamber pressure is low enough to promote turbulence in the expanding gases.

Figures 2 and 3 illustrate the preliminary results of tests to establish the ignition characteristics of a commercial detector for which a relatively short reaction zone is obtained. In this case, the flame is quenched in the premixed region by the metallic jet. A nonmetallic jet tip will, of course, extend the lower flow rate limit because it does not possess any major conductive heat transfer properties.

Another important aspect of flame combustion characteristics not shown in Figure 3 is the detachment of the flame from the jet tip. At high chamber pressures, the flame exhibits the normal conical shape with an approximate height of 0.125 inches. As chamber pressure and hydrogen flow rate are reduced, the flame height is shortened correspondingly. At a chamber pressure of approximately 300 torr, the flame detaches itself from the jet tip. Further reductions in chamber pressure and hydrogen flow rate diminish the flame height still further and the detachment distance is increased. At chamber pressures near 100 torr, the flame height and the detachment distance are both approximately 0.06 inches. The flame diameter was approximately that of the jet tip, 0.025 inches, and thus assumes a more hemispherical than conical shape.

FIGURE 2

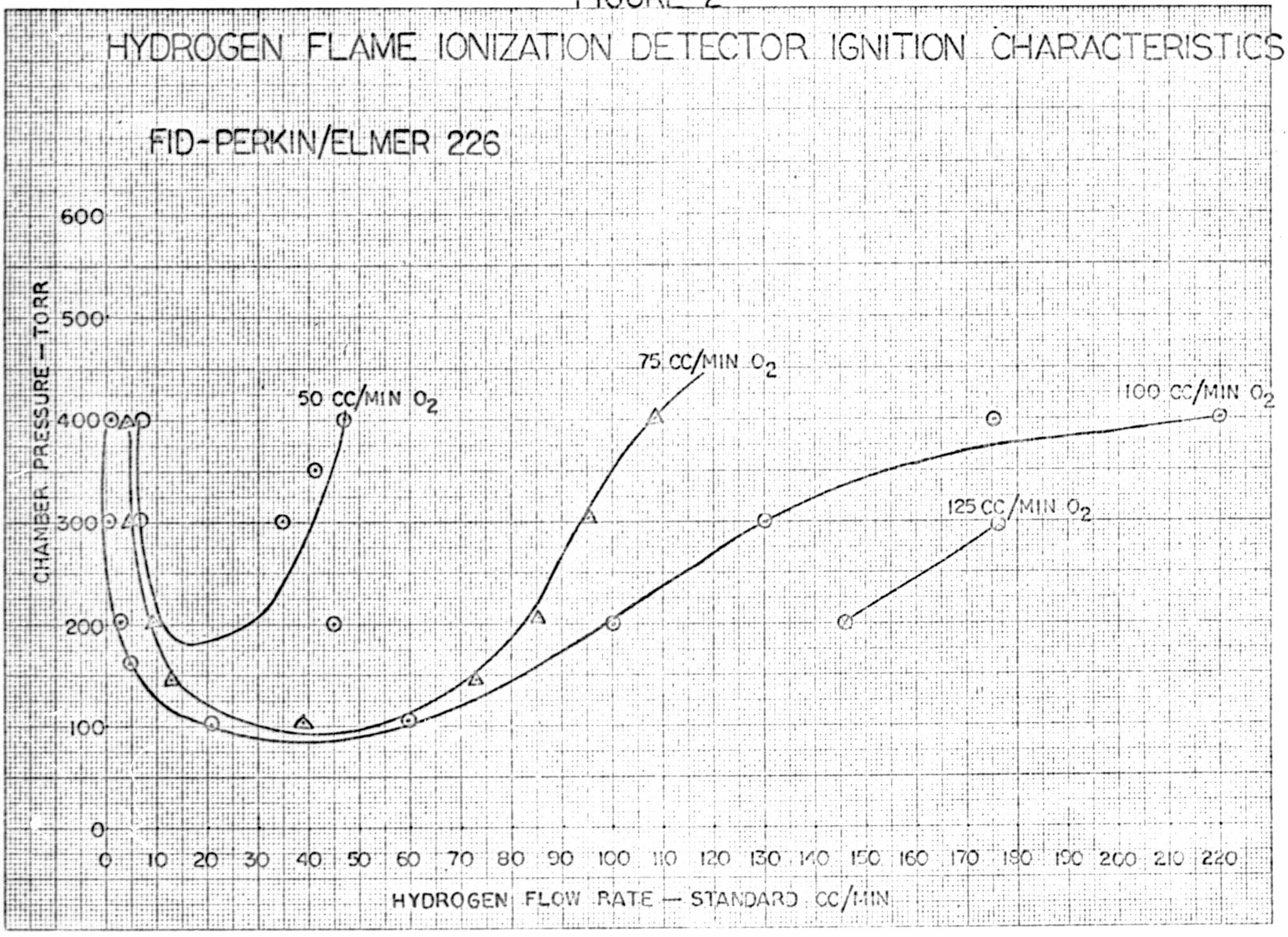
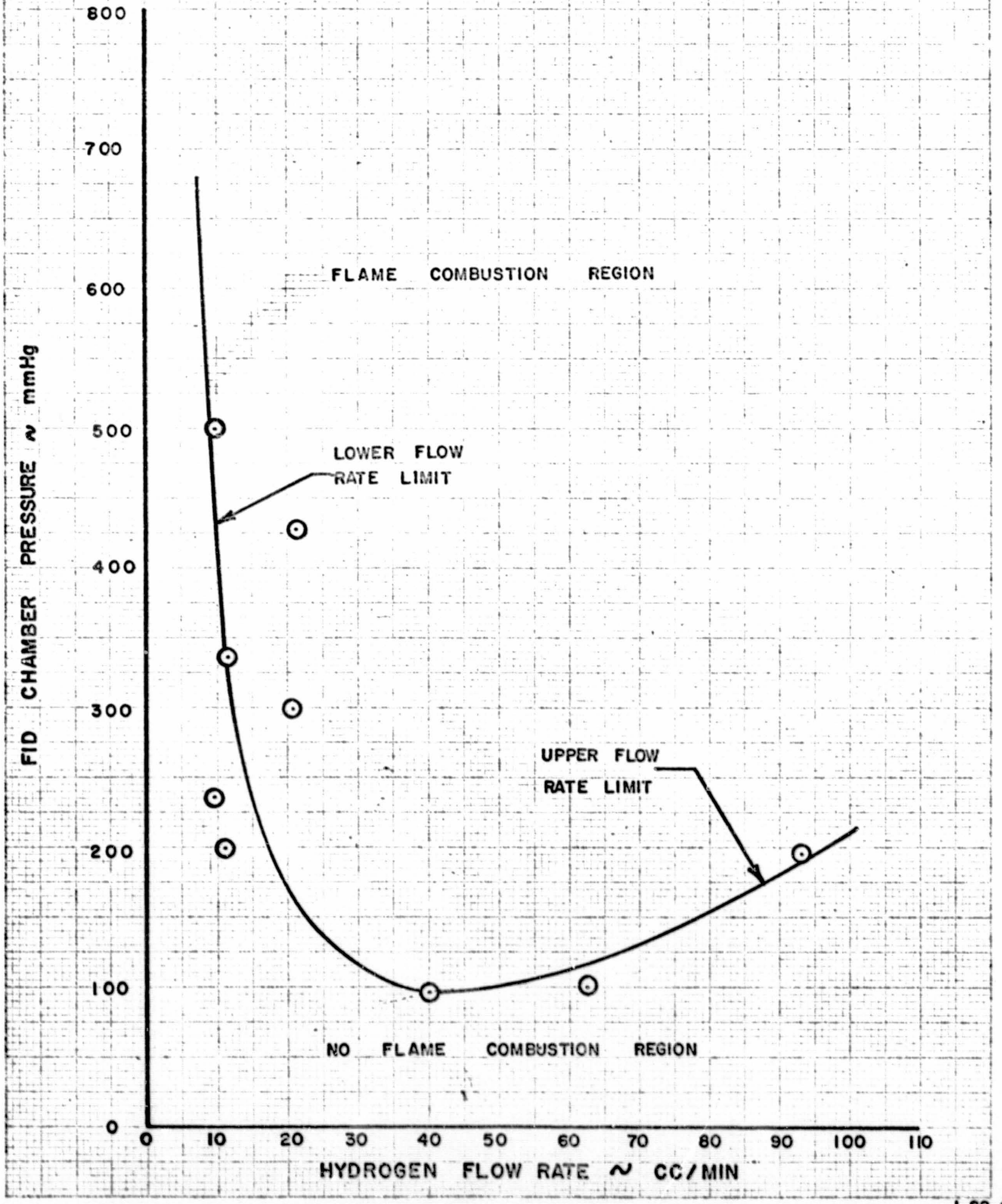

HYDROGEN FLAME IONIZATION DETECTOR IGNITION CHARACTERISTICS
FID-PERKIN/ELMER 226
CHAMBER PRESSURE — TORR
600
500
400
300
200
100
0
50 CC/MIN O_2
75 CC/MIN O_2
100 CC/MIN O_2
125 CC/MIN O_2
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220
HYDROGEN FLOW RATE — STANDARD CC/MIN

FIGURE 3

FID FLAME COMBUSTION CHARACTERISTICS

OXYGEN/HYDROGEN FLOW RATE RATIO - 4:1



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FID OPERATION WITH PRESSURIZED COMBUSTION CHAMBER

The ignition and flame combustion pressure characteristics of FID units establish to a large degree the design constraints of the chamber. Figures 2 and 3 establish the lower pressure limit at 190 and 100 torr for ignition and flame combustion, respectively. Therefore, the chamber pressure and vent port characteristics are constrained to these performance limits. It may be desirable to operate the FID at higher chamber pressures in order to attain larger flames with correspondingly larger signals and the capacity to ionize more of the hydrocarbon sample.

Pressurization of the FID chamber is accomplished by increasing the total gas flow rate in the chamber and/or by incorporating a restrictor at the chamber exit. Figure 4 graphically illustrates the relationship between the length, diameter, flow rate, and pressure drop of a capillary restrictor. Since weight, space, and ease of operation are prime factors in the design of the FID unit, a restrictor diameter below 0.015 inches will be required to maintain its length to a few inches. Two restrictors, comprised of 0.010 and 0.006-inch tubes were fabricated and assembled. Tests were then conducted to assess the detector. The detector failed to ignite completely below chamber pressures of 150 mm Hg. Other ignition failure limits were established at lower and upper hydrogen gas flow rates. The upper limit was established by a gas velocity which exceeded the flame-front velocity. The temperature of the ignitor surface may also have been too low to supply sufficient power to the gas. The lower limit in the lower chamber pressure regions also

failed to ignite for the identical reasons. At higher chamber pressures, ignition failure was primarily due to the unavailability of combustible mixtures inside the compositional flammability limits.

The shape and limits of the ignition region can be significantly changed by relocating the ignitor. Thus, dependency on the chamber pressure, the location of the ignitor and its relationship to the gas velocity profile within the chamber are important design considerations.

FLAME COMBUSTION CHARACTERISTICS AT REDUCED PRESSURES

The size and shape of the flame are established by the hydrogen flow rate, chamber pressure, and the flame holder shape. Figure 3 illustrates the preliminary results of tests to establish some of the flame combustion characteristics of a commercial detector employing a circular jet tip. A flame cannot be sustained at chamber pressures below 100 mm Hg. As chamber pressure is increased, larger hydrogen flow rates are required to sustain a flame.

The upper flow rate limit is established by the maximum hydrogen gas velocity prior to exceeding the flame-front velocity. As the hydrogen flow rate is increased, the gas velocity increases and eventually, the flame is blown away. This condition arises from the nature and structure of diffusion flames which possess a premixed flame structure at the base of the flame adjacent to the rim of the jet tip. Consequently, this region will exhibit a flame-front velocity which propagates in a direction opposite to that of the jet gas velocity. In

the lower FID chamber pressure region of the lower flow rate limit, the flame is blown away for identical reasons. However, at the higher FID pressures of the lower flow rate limit, the flame is severely reduced in height to ignition and flame combustion characteristics of the FID chamber.

Fundamental problems were introduced to the detector when it was operated with a pressurized unit. It is certain that the equilibrium partial pressure of oxygen, helium and water vapor in the chamber will be proportional to the respective gas flow rates. Thus, operation at gas flow rates suitable for an open detector will yield water vapor mole fraction between 0.30 and 0.35. This gas composition is not conducive to sustaining a stable flame. According to mass action considerations, the flame combustion process rate should be diminished.

The FID vent port characteristics are illustrated by Figure 4. Operation at chamber pressures above 25 mb will result in a pressure ratio at the port exit above the critical valve and, therefore, an exhaust gas Mach Number of 1. The vent port line length required to achieve the required flow restriction and pressure drop is given by the equation below:

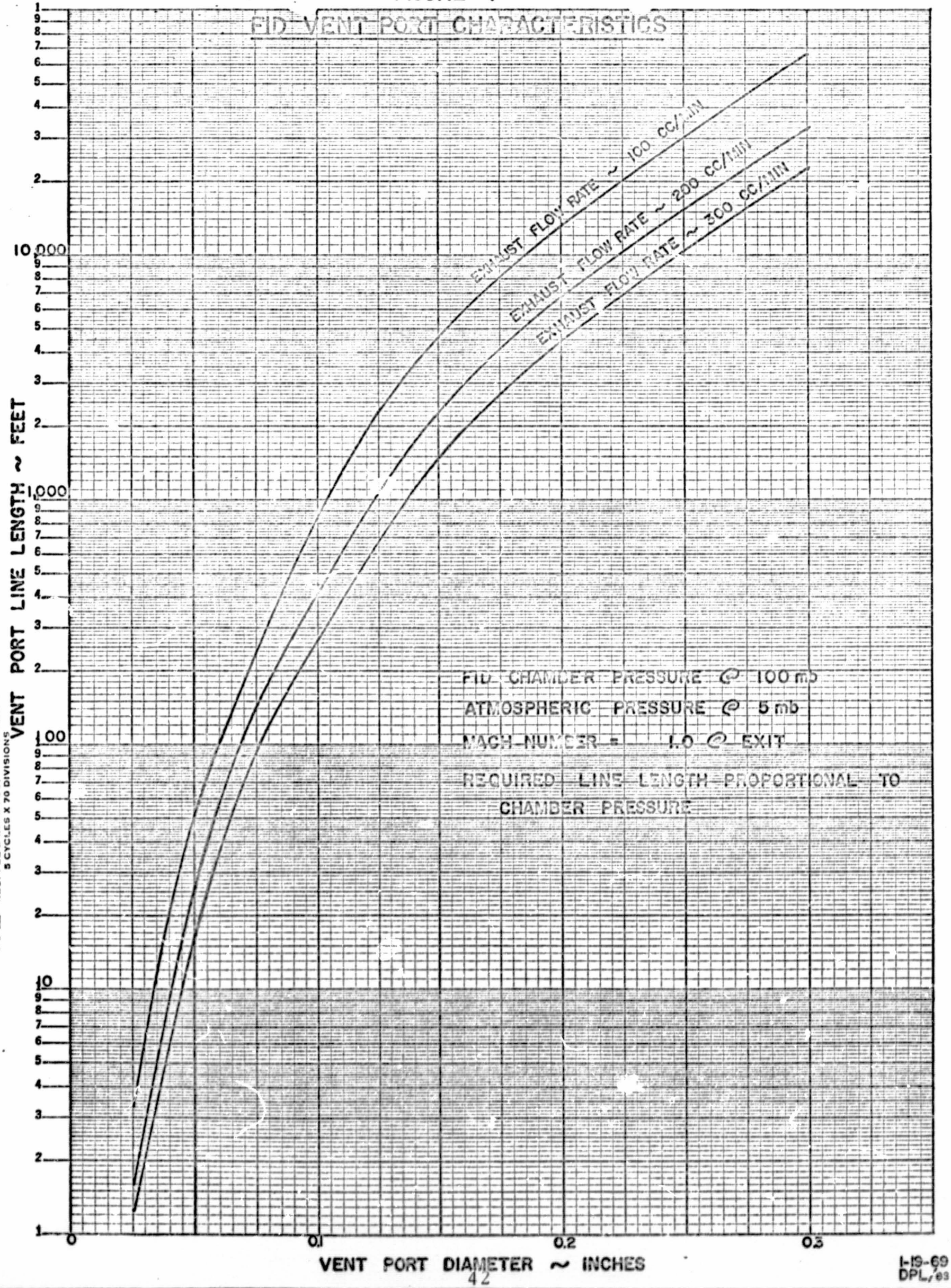
$$L = \Delta P \quad 39.6 \gamma D^5 / f(w)^2,$$

L = vent line length, FT,

γ = exhaust gas density, lb/FT^3

f = gas friction factor, dimensionless,

FIGURE 4


FID VENT PORT CHARACTERISTICS
EXHAUST FLOW RATE ~ 100 CC/MIN
EXHAUST FLOW RATE ~ 200 CC/MIN
EXHAUST FLOW RATE ~ 300 CC/MIN
FID CHAMBER PRESSURE @ 100 mb
ATMOSPHERIC PRESSURE @ 5 mb
MACH NUMBER = 1.0 @ EXIT
REQUIRED LINE LENGTH PROPORTIONAL TO CHAMBER PRESSURE
VENT PORT LINE LENGTH ~ FEET
10,000
1,000
100
10
1
0
0.1
0.2
0.3
VENT PORT DIAMETER ~ INCHES
5 CYCLES X 70 DIVISIONS
1-19-69
DPL/93

w = exhaust gas flow rate, lb/sec,

ΔP = pressure drop through vent line, lb/FT^2

D = vent line diameter, FT,

A vent (0.025-inch diameter) exhausting gas at the rate of 100 cc/min. will require 3.3, 6.6, and 9.9 feet of line to promote chamber pressures of 100, 200, and 300 torr, respectively. This appears to be an excessive amount of tubing for such a small diameter. It can be incorporated into the design only by increasing the FID chamber dimensions. A chamber with a 1-inch inside diameter will require approximately 1.5, 1, and 0.5 inches of stacked coils to produce a chamber pressure of 100, 200, and 300 torr, respectively.

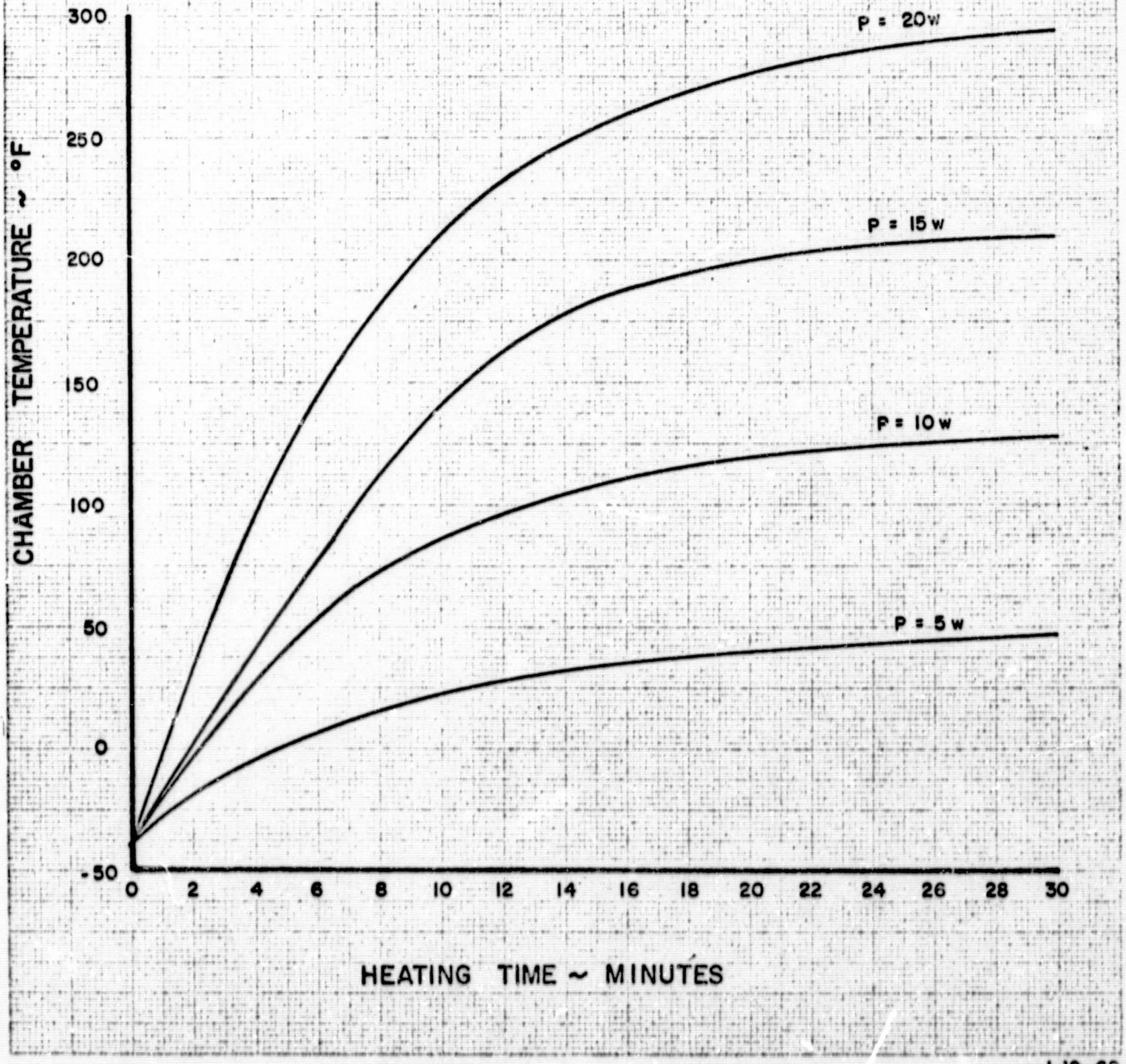
An alternate method of providing the flow restriction is that which utilizes a porous metal plate as one side or end of the chamber. This type of restrictor has the definite advantage of providing a more uniform flow path over a relatively wide area.

Heat losses will increase by 0.00114 $W/^oF$ above the environmental temperature or approximately 0.75 W when the chamber temperature is 126° F and the environmental temperature is -40° F. Figure 5 illustrates the thermal characteristics of this detector.

FIGURE 5

FID CHAMBER THERMAL TIME RATE OF RESPONSE CHARACTERISTICS

FID CONDUCTANCE TO ENVIRONMENT - 0.2 BTU/HR-°F
FID UNIT WEIGHT - 0.14 LBS
TEMPERATURE LEVEL PROPORTIONAL TO ENVIRONMENTAL TEMPERATURE
ENVIRONMENTAL TEMPERATURE ~ -40°F
STEADY STATE POWER REQUIRED = 0.039 w/°F



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VI. PRE-PROTOTYPE DETECTOR AND TESTS

ATC DETECTOR DESCRIPTION

The pre-prototype detector was fabricated primarily from aluminum with teflon or KEL-F seals at the mechanical interfaces.

Figure 6 is a sketch of the detector and Figures 7 and 8 are photographs of the unit used in this study. The detector has two curved-plate electrodes. The hot wire ignitor is placed near the wall about 1 inch above the jet tip. All electrical connections and both gas connections are routed through the base of the detector. The oxygen inlet terminates as it enters the base. The oxygen is then dumped into a chamber below the base, which is ringed with holes to allow the oxygen to diffuse upward and around the jet tip.

The detector's top cap is removable and has a 7-cm, 0.010-inch capillary restrictor venting the gases to the atmosphere. The pressure drop across the restrictor is about 0.7 atmospheres at environmental vacuum.

A number of compromises were necessary in the detector design because the schedule did not permit the incorporation of long-lead items or processes. The compromises that were made did not adversely affect the principal goal of operating the detector under pressure, but should be avoided in future models. The following are the recommended changes:

1. Glass headers for electrical and gas connections.

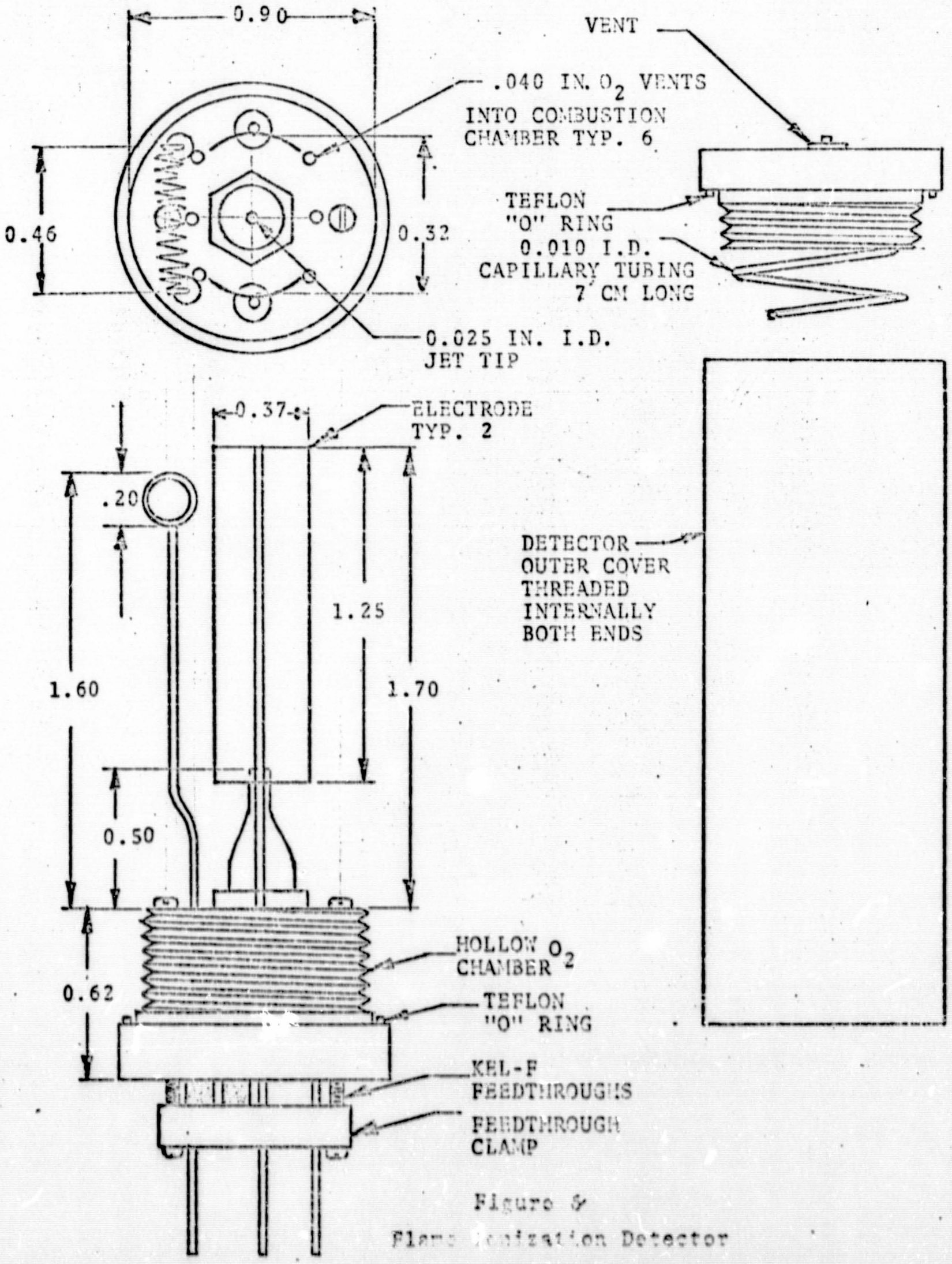

Figure 8

Flame Ionization Detector

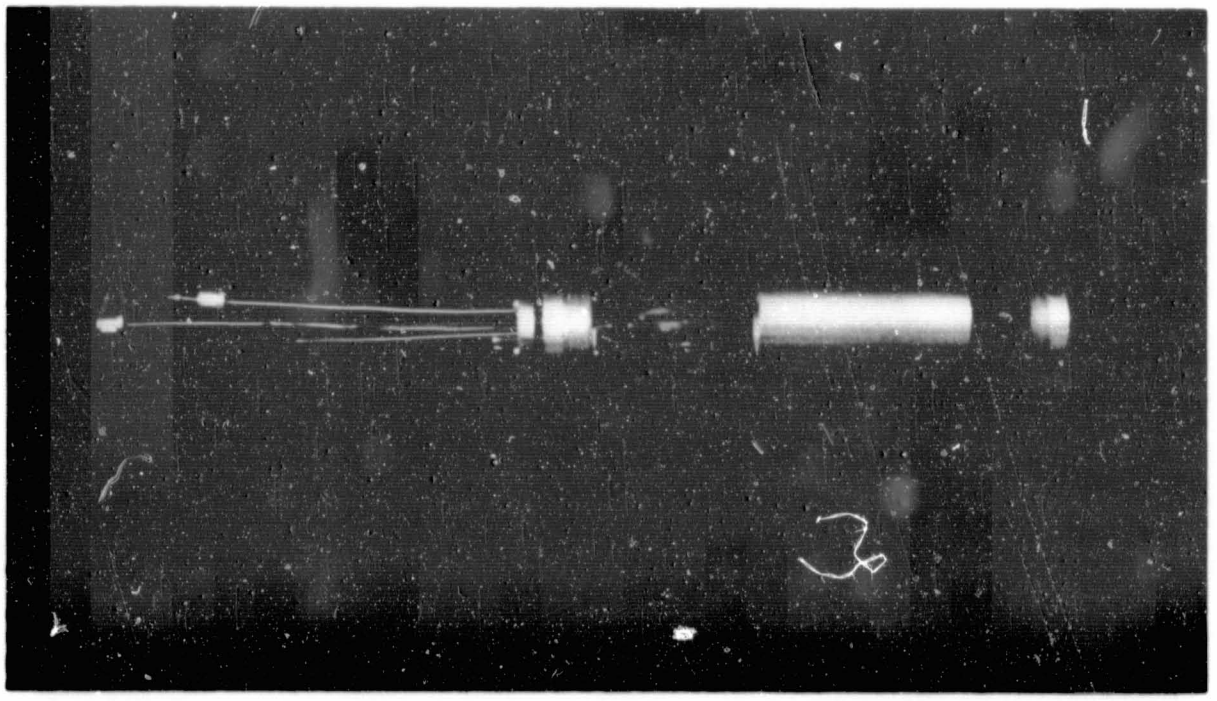

Figure 7 Pre-Prototype Detector Disassembled

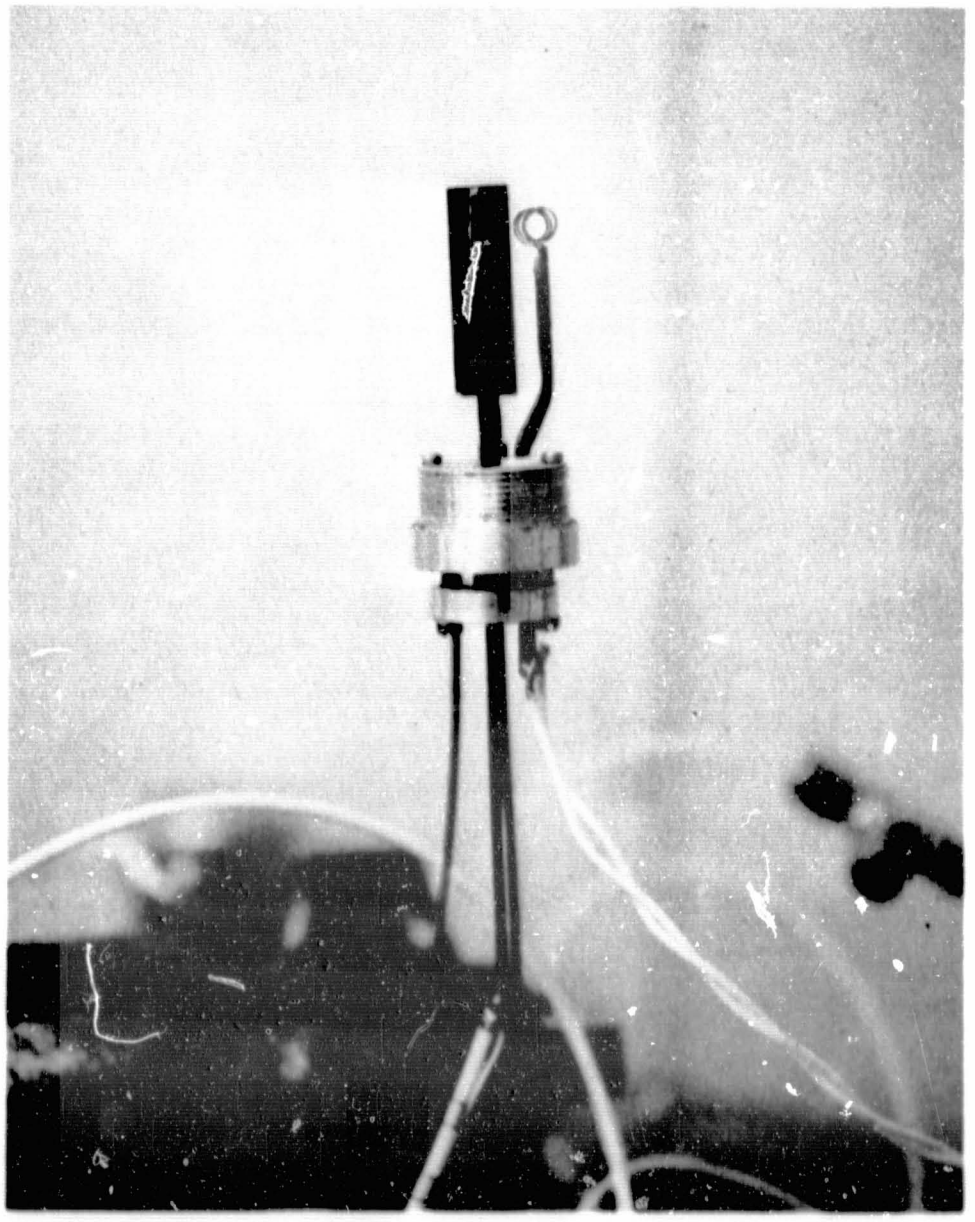

Figure 8 Pre-Prototype Detector Installed for Testing

2. Plated or anodized aluminum.
3. Insulated jet tips.
4. Porous metal vent.
5. Replaceable jet tips.
6. Replaceable electrodes.

DETECTOR TEST SUMMARY

The following is a brief summary of results of tests conducted on the pre-prototype detector. Figures 9 and 10 are photographs of the detector vacuum test setup. The principal problem during the testing was the maintenance of leak-tight mechanical interfaces.

A. Sensitivity

At 760 torr (1 atmosphere) environmental pressure and temperature stabilized at 153° C at top of detector and 120° C at bottom of detector after 5 minutes of operation, the sensitivity measured was

$$0.17 \frac{C}{g\text{-atm } C}$$

B. Internal Ignition Pressure at Environmental Pressure of 1 Earth Atmosphere

At vent-cap temerature of 160° C (attained after 5 minutes of operation), detector ignited and sustained flame for internal pressure of 2.3 atmospheres or greater.

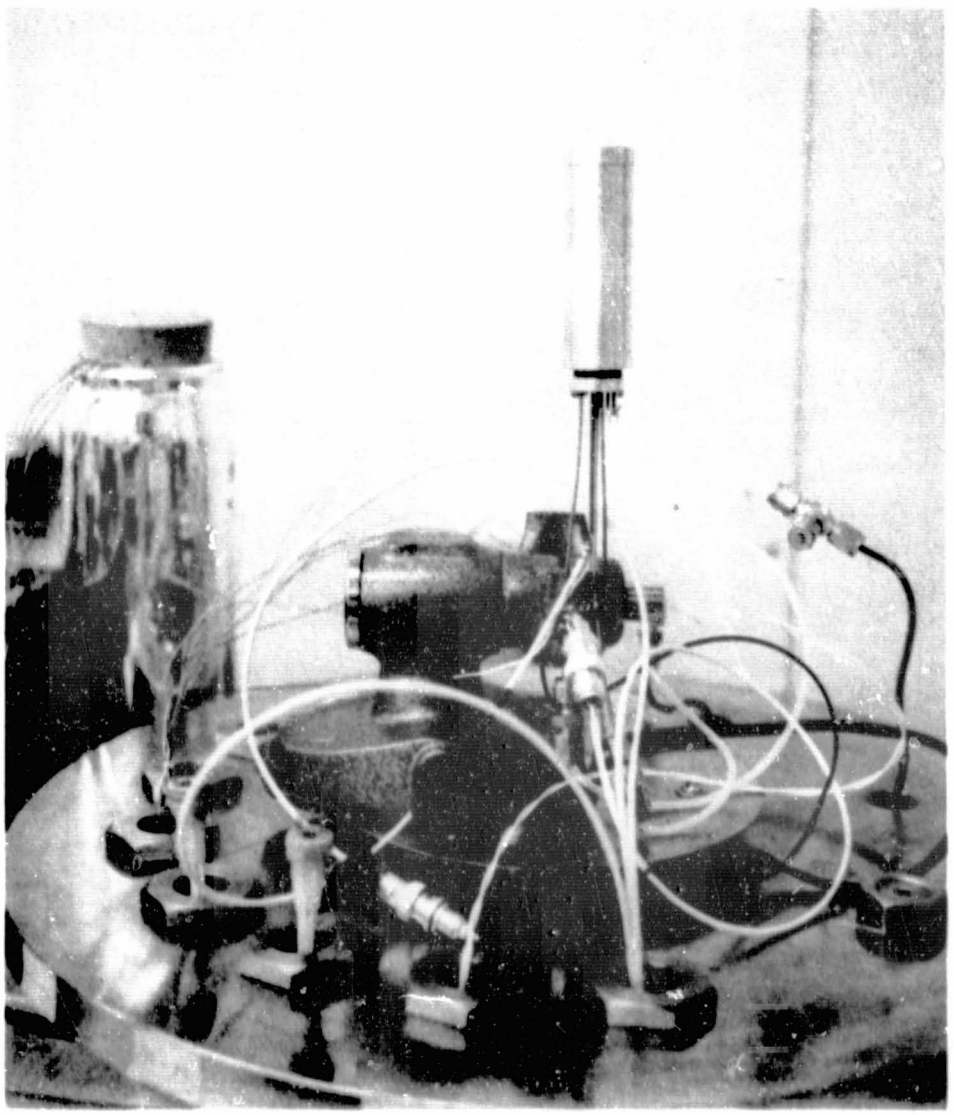

Figure 9 Pre-Prototype Detector in Vacuum Test Fixture

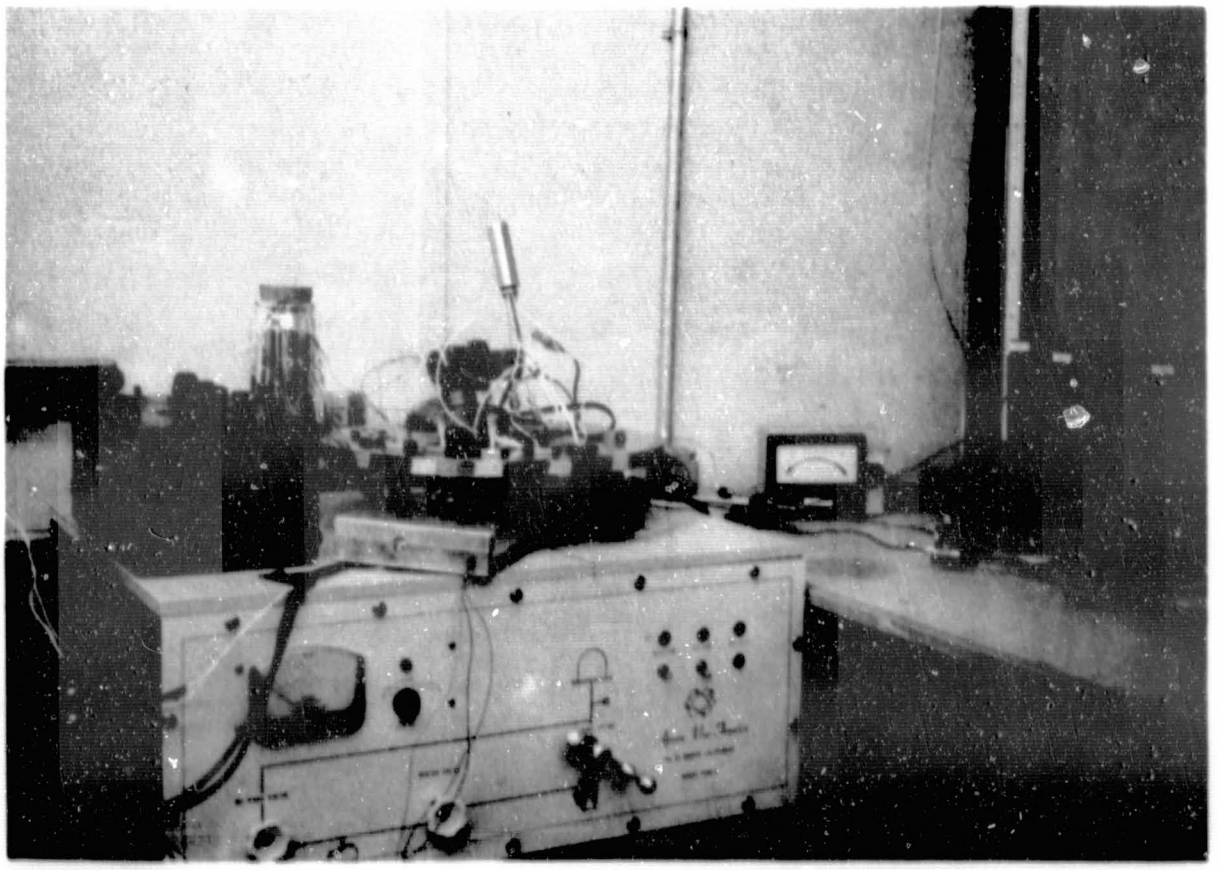

Figure 10 Pre-Prototype Detector Vacuum Test Installation

C. Ignition Threshold Under Varying Environmental Pressure

1. At 400-torr internal pressure and vent-cap temperature of 130° C, detector ignited at pressures down to 200 torr and sustained flame down to pressures as low as 3 torr.

2. At 400-torr internal pressure and vent-cap temperature of 170° C, detector ignited and sustained flame at pressures as low as 3 torr.

VII. GAS SYSTEM AND PYROLYSIS STUDIES

The gas-handling and pneumatic system, the sample injection system, and the pyrolyzer were examined only briefly before it became apparent that an extremely thorough investigation of the flame ionization detector deserved to be given priority. Several means for supplying gases and injecting samples into the pyrolyzer were studied, and the results are described here.

The first method considered for supplying gases was a self-generating system where water is either electrolyzed or some chemically active compound, such as lithium hydroxide, is added. In this manner, hydrogen and oxygen gases are produced within the system, and savings in weight of pressure vessels, valves, and gas conduits result. However, two primary design problems related to the continual production of gases and the achievement of high pressures are associated with self-generating systems. Nevertheless, it appears that the pressure of the gases produced could be sufficiently high, if the detector system is operated at reduced pressures. If helium or some other diluent gas is required, it will probably be stored and mixed into the self-generated gases.

A second means of providing gases is to carry a combustible mixture with the detector system and feed it directly into the flame detector. This system, however, has the disadvantages of a high explosion hazard and a detector operating with a premixed flame.

Gases can also be furnished by carrying the hydrogen and oxygen separately in supply tanks and feeding them into the hydrogen flame detector. Optimum hydrogen and oxygen flow rates and delivery pressures can easily be achieved with valves, regulators, and a mixing chamber. This, of course, is accomplished at the expense of a weight penalty.

Several means of injecting a sample into the pyrolyzer were also investigated. A device comprised of a helical rotating screw enclosed by a cylindrical sleeve appears to be adequate. It processes and transports the soil to the pyrolyzer and indicates when it is filled. The major problems associated with it are jamming of the screw and integration with the pyrolyzer.

An integrated pneumatic sample acquisition and sample injection system was also examined. Although its mechanical moving parts were reduced to those concerned only with deployment and alignment, it seriously limited the acquisition of surface layer samples consisting only of fine dust. A relatively large pressurized gas supply with the attendant penumatic system and controls is also required.

The requirements of the pyrolysis chamber were investigated to help define the number of analyses to be conducted, the average size of the soil sample and the chamber design and configuration. Sample injection indicators, chamber sealing methods, and chamber heating techniques were conceived and preliminary calculations were made to establish their feasibility and performance characteristics.

VIII. CONCLUSIONS

This study has resulted in the unification of hydrogen flame ionization detector technology and the fabrication of a pre-prototype detector which ignites and sustains a flame in a vacuum. Its sensitivity is equivalent to the best commercial detectors available and ignition characteristics are superior.

The detector, however, is not ready to be utilized for carbon analysis in the Mars Lander. Detector operation in a pressurized chamber imparts undesirable characteristics associated with flame noise and stability due to internal aerodynamic disturbances and water condensation.

The study has established with a reasonable degree of certainty the fundamental changes which must be made to the detector and its elements: the jet tip, the electrodes, gas delivery modes, and the internal aerodynamic design. In addition, the study has permitted the definition of a preliminary design and the technical problems underlying the development of a spaceworthy prototype flight detector.

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